

# Ignition Delay Time and Laminar Flame Speed Measurements of a Li-ion Battery Electrolyte: Ethyl-Methyl-Carbonate

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## 1 Introduction

To mitigate climate change and reduce pollution in cities, several countries in the world have set laws to ban internal combustion engine (ICE) vehicles from cities or prohibited sales of new ICE vehicles within 10-20 years. In addition, several vehicle brands are planning to go fully electric within the next decade. Nowadays, and for at least the decade to come, these electric vehicles use lithium-ion batteries (LIB) to store their energy. In a LIB, lithium salt ions move between the anode and the cathode during the charge/discharge cycles via a liquid electrolyte and through a separator. The liquid electrolyte is a mixture of various organic solvents, linear and cyclic carbonates for the most part. These carbonates are highly flammable [1], and they are the reason why electric vehicles might burn after an accident or a defect in the battery conception or fabrication.

With a fast-growing number of electric vehicles on the roads, a higher number of collisions involving electric vehicles is to be expected. If the collision is severe enough, the battery can suffer mechanical abuse, which potentially leads to electrical abuse followed by temperature abuse and then fire [2].

To better control LIB fires, it is therefore necessary to understand the details of the combustion chemistry of the electrolyte's components. Among these electrolytes, only linear carbonates have been investigated. More specifically, Di-Methyl-carbonate (DMC) [3-7] and Di-Ethyl-carbonate (DEC) [8-12] were studied, as they are also considered promising biofuels. On the other hand, except the very recent studies from Maruta et al. [13, 14], where a detailed kinetic model is proposed, there is no study for ethyl-methyl-carbonate (EMC).

The goal of this study was to provide new kinetics data for EMC, to further develop this model. To this aim, ignition delay times ( $\tau_{\text{ign}}$ ) of EMC/air mixtures were measured in a heated shock tube (100°C) for three equivalence ratios ( $\phi$ ): 0.5, 1.0, and 2.0 at near atmospheric pressure. These data were complemented by an equivalence ratio sweep of laminar flame speed measurements at 1 atm and an initial temperature of 130°C. The Takahashi et al. [14] model was used to predict these data.

## 2 Experimental methods

### 2.1 Shock tube and ignition delay time measurements

Ignition delay time measurements were performed in a stainless-steel shock tube (15.24-cm i.d., 4.72-m long and 7.62-cm i.d., 2.46-m long for the driven and driver sections, respectively). The shock tube was in a single-diaphragm configuration, and two polycarbonate diaphragms (0.25- and 0.13-mm thickness) were used for each experiment. The mixing tank, manifold, and driven section of the shock tube were heated to 373 K. The velocity of the incident shock wave was measured using five PCB-113B22 piezoelectric pressure transducers. This velocity was then extrapolated to the endwall to determine post reflected-shock conditions, with a temperature uncertainty behind reflected shock waves ( $T_5$ ) below 10 K. Test pressure was monitored on the sidewall (16 mm from the endwall, Kisler 603-B1) and on the endwall (PCB-113B22). Chemiluminescence from  $\text{OH}^*$  was recorded at both these locations using an interference filter at  $307 \pm 10$  nm. The test section was evacuated to  $2 \times 10^{-5}$  Torr or better using a roughing pump and a turbomolecular pump before each experiment. The ignition delay time was measured using the  $\text{OH}^*$  signal from the endwall with the endwall pressure signal to determined time zero, as described in Fig. 1. The uncertainty on these measurements is estimated to be about 10%. Test mixtures were prepared manometrically in a stainless-steel mixing tank using premixed air (certified 21%  $\text{O}_2$ , 79%  $\text{N}_2$ , Praxair, 99.999%), and Ethyl-Methyl Carbonate (99%, Sigma Aldrich). The fuel was introduced into the tank via a heated vial. The vial was degassed at least 3 times prior to introducing the fuel into the mixing tank.

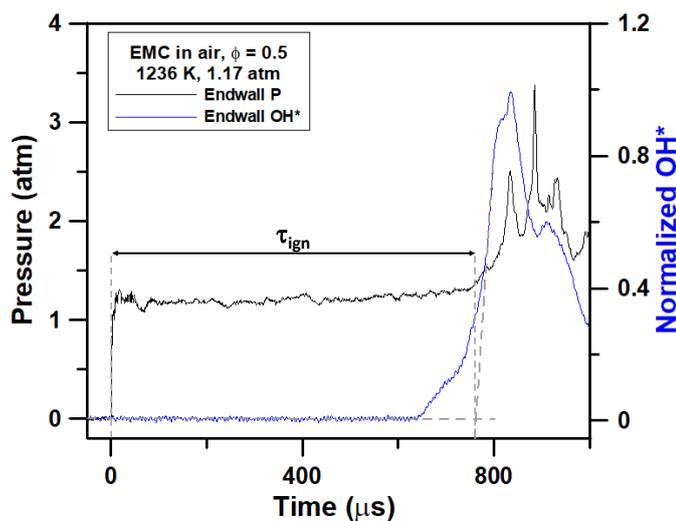


Figure 1: Determination method for the ignition delay time.

### 2.2 Closed vessel and laminar flame speed measurements

Laminar flame speeds of EMC at various equivalence ratios were measured using a spherically expanding flame in a stainless-steel cylindrical chamber (31.8-cm i.d. and 27.9-cm length), with an optical access of 12.7 cm in diameter. In this study, the entire apparatus was heated to 130°C using a heating jacket with a temperature uniformity of  $\pm 1$  °C. A schlieren diagnostic was used to track the flame propagation, and flame-front-tracking software was developed in-house to extract flame radii from the schlieren images using contrast adjustment and Canny edge detection. The rate of change of the flame radius is determined from the time history of the flame radius. Using known nonlinear extrapolation

methods, the data were fitted and then extrapolated back to zero stretch, giving the burned, unstretched flame speed [15].

Mixture densities were calculated using the Takahashi model [14] and the equilibrium chemistry routine in Chemkin-Pro. To prepare the mixture, a known amount of EMC (weighed) was injected directly into the vessel and allowed to fully vaporize for 30 minutes. Air (21% O<sub>2</sub>/79% N<sub>2</sub> certified, 99.999% gas purity, Praxair) was then added up to atmospheric pressure. The final mixture was allowed to mix for at least 10 minutes before running the experiment.

### 3 Results and Comparison with Models

#### 3.1 Ignition delay time measurements

Figure 2 presents the ignition delay time results along with the model comparisons. The three equivalence ratios investigated are compared in Fig. 2(a). As one can see, there is basically no effect of the equivalence ratio on the ignition delay time of the EMC/air mixtures under our conditions. The comparison with the Takahashi model is visible in Fig. 2 (b)-(d) for  $\phi = 0.5$ , 1.0, and 2.0, respectively. This comparison shows that the model is in an overall good agreement with the data. At  $\phi = 0.5$ , the predicted ignition delay times are too long by a factor of around 1.5 over the entire range of temperature investigated. For the stoichiometric case, Fig. 2(c), the reactivity is better predicted, especially for the highest temperatures investigated. On the other hand, the model also rapidly diverges below 1300 K, and a difference factor of about 2 is observed for the lowest temperature investigated. Finally, for the fuel-rich case, the same discrepancy by a factor of about 2 is also observed for the lowest temperature, but the difference between the model and the data is relatively moderate above 1300 K, with an overprediction of the ignition delay time by about 30-50%.

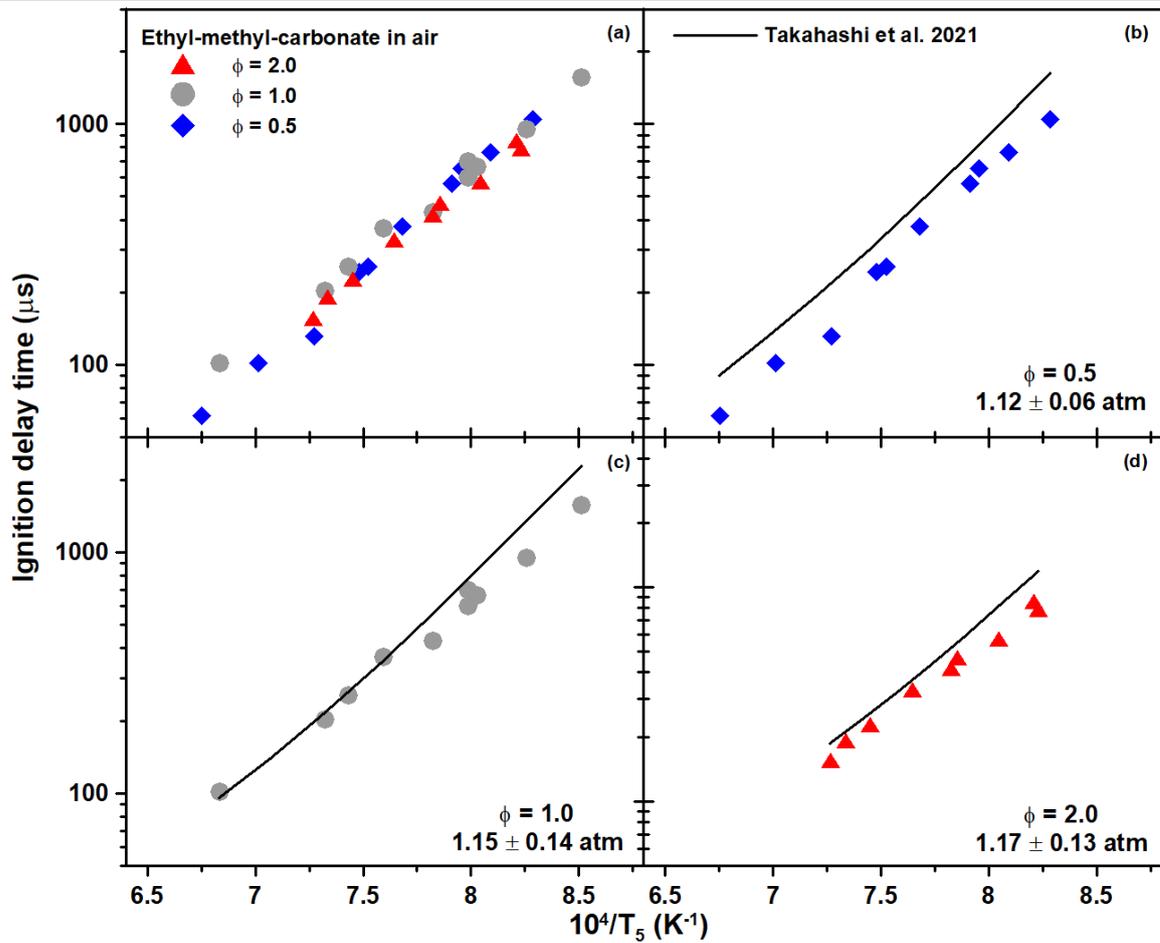


Figure 2: Ignition delay time of Ethyl-Methyl-Carbonate in air and comparisons with the model from Takahashi et al. [14].

### 3.2 Laminar flame speed measurements

The laminar flame speed of EMC is visible in Fig. 3. Like most hydrocarbons, the maximum flame speed (54.4 cm/s) is found around an equivalence ratio of 1.1. The comparison with the Takahashi model shows that the experimental data tend to be lower than the model's predictions, although the model is accurate at the equivalence ratio extremities investigated. However, it is worth mentioning that the model's predictions are well within the experimental uncertainties (5%).

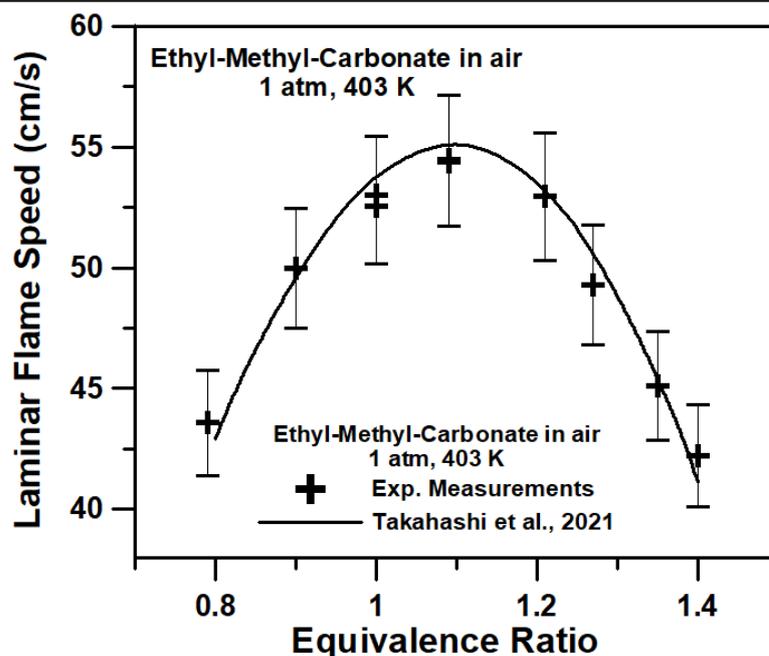


Figure 3: Laminar flame speed of Ethyl-Methyl-Carbonate in air at 1 atm and an initial temperature of 403 K.

## 4 Conclusion

EMC is an important component of the electrolyte used in a Li-ion battery. The combustion chemistry of this flammable carbonate has been investigated in one study only, by Takahashi and coworkers [14]. To further validate the detailed kinetics model of EMC, new experiments were performed during this study. To the best of the authors' knowledge, the ignition delay time and laminar flame speed measurements presented herein are the only measurements of this type for this molecule. The recent model, while not validated for these conditions, predicts the data with an overall good accuracy. It was found that the laminar flame speed predictions were slightly too high, and the predicted ignition delay times were marginally too large. Future work will try to improve the accuracy of this model using the present data.

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